

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

**0 402 554
A1**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 89810440.1

(51) Int. Cl.⁵: H01M 4/60, H01M 10/40

(22) Date of filing: 12.06.89

(43) Date of publication of application:
19.12.90 Bulletin 90/51

(84) Designated Contracting States:
DE FR GB IT

(71) Applicant: **HONDA GIKEN KOGYO KABUSHIKI
KAISHA**
1-1, 2-chome Minami-Aoyama
Minato-ku Tokyo(JP)

(72) Inventor: **Müller, Klaus**
6, Chemin Jules-Vuy
CH-1227 Carouge/Genève(CH)
Inventor: **Kulhanek, Antonin**
47, Avenue du Lignon
CH-1219 Le Lignon/Genève(CH)

(74) Representative: **Dousse, Blasco et al**
7, route de Drize
CH-1227 Carouge/Genève(CH)

(54) Rechargeable storage battery with electroactive organic polymer electrodes in polar solvent electrolyte.

(57) Cells are disclosed using doped electroconductive polymer electrodes and electrolytes of alkali metal cations and soft anions in polar organic solvents. The structure of the negative electrodes comprises layers of electroconductive polymers and ion-exchange resin. Conditioning the negative electrodes is effected with AC current, the energy of the negative pulses exceeding that of the positive pulses.

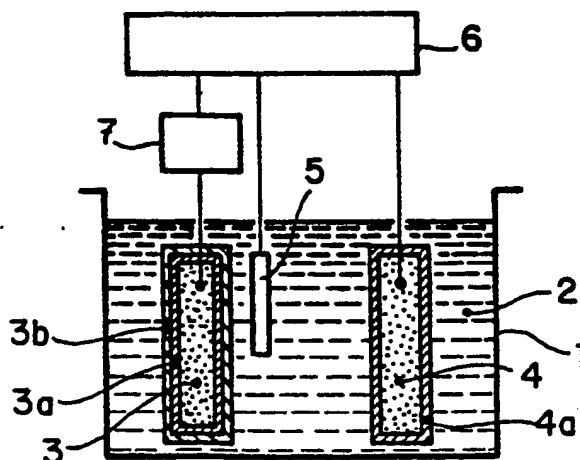


FIG. 1

EP 0 402 554 A1

RECHARGEABLE STORAGE BATTERY WITH ELECTROACTIVE ORGANIC POLYMER ELECTRODES IN POLAR SOLVENT ELECTROLYTE

The present invention concerns rechargeable batteries and, more particularly, batteries whose electrodes involve conjugated electroconductive organic polymers, as well as a method for conditioning such polymer electrodes.

It is well known that all batteries are formed of a plurality of cells each including at least two electrodes, a negative electrode (defined as the anode) and a positive electrode (defined as the cathode), both being immersed in an ionic conducting liquid (the electrolyte). During discharge of the cell, the electrons leave the anode, flow through an external circuit connected to the electrodes where they do work, and return to the cell via the cathode whose positive charge is thus progressively neutralized. This process continues until an equilibrium is reached, i.e. until when the electron donating substances (at the anode) and electron acceptor substances (at the cathode) are consumed, or when an opposing potential arises at the electrodes due to the presence in the electrolyte of the electrooxidized and corresponding electroreduced products which are formed in the reaction.

For instance in the classical nickel/cadmium battery in which the cadmium is the anode and nickel oxide is the cathode, the cadmium spontaneously dissolves to cadmium ions Cd^{+2} giving up electrons to the external circuit while the nickel oxide (Ni^{III}) is reduced to Ni^{II} by the incoming electrons. In the electrolyte (aqueous alkali hydroxide), the negative charges are carried toward the cadmium electrode by the hydroxy anions (whence the name anode) whereas the positive Cd^{+2} cations move toward the other electrode (whence named the cathode).

In recharging, the reverse operations take place: the Cd^{+2} cations travel the opposite way in the electrolyte to be reduced back to metallic cadmium at the negative electrode (which is defined then as a cathode), while the negative OH^- anions go back to the nickel electrode (the anode in this case) where they reoxidize Ni^{II} to Ni^{III} . Hence the operation of the Ni/Cd battery involves chemical consumption of electroactive substances in discharge and, upon recharging the original substances are reformed from the thus chemically modified species, e.g. the cadmium metal is plated out of the cadmium ions solution. Now, cadmium is very toxic and undesirable; however when replaced by zinc, the reversibility of the above operations is sometimes awkward (dendrite formation) and the number of charge and discharge cycles is rather limited; hence batteries using polymer electrodes not subjected to periodical consumption and ref-

ormation of electroactive materials are attractive because of their inherent reversibility and prolonged lifetime.

For instance in cells involving carbon, polyacetylene (or other conjugated electroconductive polymers) electrodes and an alkali salt e.g. LiClO_4 in a non-aqueous solvent as the electrolyte, the following events occur when charging: the generator pumps off electrons from the positive electrode and drives them through the external circuit to the negative electrode where they "equilibrate" (the electrode is doped) with the positive Li^+ cations from the electrolyte. Simultaneously the positive "holes" in the positive electrode are neutralized and thus the electrode is doped with ClO_4^- anions. During discharge the reverse effect takes place.

Among the organic electroconductive polymers, polypyrrole is a favoured one because of its long recycling life and easy electrochemical or chemical preparation. So many battery systems involving polypyrrole (pPy) have been reported. Many are hybrid systems in which the positive electrode comprises polypyrrole and the negative electrode is made of an electropositive consumable metal such as alkali metals, metals of groups II and III of the Periodical Table or alloys thereof, (see EP-A-199 175; ALLIED CORP). For illustration, some prior art references are briefly reviewed below.

For instance, Japanese document 60-225 376 (1985) application JP-59/82316, TOYOTA MOTOR CORP., discloses a positive electrode made of carbon fibers coated with pPy or polythiophene and, optionally, other conductive materials such as gold, copper, silver, In_2O_3 , SnO_2 and the like. For making a cell, an Al counterelectrode is used in a LiClO_4 /acetonitrile solution. On charge, the lithium deposits on the negative electrode while the positive pPy electrode dopes with ClO_4^- ions. A cell with open voltage of 2.5-3 volt is thus obtained (the lithium anode is about 2-2.5 volt below the Ag/AgCl reference couple).

Japanese document 62-170150 (1987), application No 59-10808 (1986), TOYOTA MOTOR CORP. discloses a battery with stacked electrode couples. The electrodes are similar to that of the previous document, the use of some further electroactive polymers being listed, e.g. polyaniline, polythiophene (polythienylene) and the like. Listed electrolytes include LiClO_4 , R_4NClO_4 , R_4NPF_6 , R_4NBF_4 (R being alkyl) in solvents like acetonitrile, propylene carbonate, benzonitrile, nitromethane, sulfolane and mixtures thereof.

The positive electrodes are manufactured from pieces of knitted carbon fibers which are dipped in 1-2 molar pyrrole/acetonitrile solution containing LiBF_4 (2 molar) and electrolyzed against an Al counterelectrode at 7 mA/cm^2 for an hour. This provides a polypyrrole coat of a few hundreds of μm on the graphite knit.

Japanese document 60-127663, TOYOTA CENTRAL INST., discloses a battery in which the cathode comprises a coat (1-1000 μm thick) of polymer blend or of copolymer of pyrrole and thiophene or alkyl derivatives thereof deposited on current collectors which can be of platinum, gold, nickel, steel, graphite, carbon and the like. The technique for depositing the polymers on the collectors is similar to that disclosed in the previous documents using an aluminium negative electrode and lithium salts in organic polar solvents as the electrolyte. Films of electroactive polymers in the range of 100 μm thickness are deposited under about 7 mA/cm^2 . Current densities around 12 mA/cm^2 or 1 mA/cm^2 are reported to be too high and too low, respectively.

Japanese application 63-253403, HONDA, discloses a secondary battery whose cathode is coated with a film layer comprising polypyrrole, a supporting salt and a cation exchange resin. The cathode is made from a substrate immersed in a solution (0.01 - 1 molar) of pyrrole, and of supporting salt and containing 2 - 200 g/l of the ion exchange resin; the solution is electrolyzed under 2 mA/cm^2 at 0.5 - 0.9 V (relative to the saturated calomel electrode (SCE) in water). The substrate can be of Pt, Au, Ni, stainless steel and the coating is actually a film of a blend of pPy, the resin (for instance a perfluorinated sulfonic acid resin like Nafion®) and the supporting salt can be LiClO_4 , LiBF_4 , Na tosylate and the like. In use, i.e. in discharge using an Al/Li anode in acetonitrile, undoping by the supporting ions occurs leaving micropores in the film layer. The system provides an output of 3 V. No use of this polymer electrode as a battery anode is reported.

In the cells disclosed in the above documents, the cathode comprises polypyrrole and the anode is of a consumable metal which periodically dissolved into the electrolyte and reprecipitates on the electrode collector substrate as recycling proceeds. As mentioned earlier, this has the drawback of questionable durability because of dendrite formation upon recharging which leads to auto-discharge conditions.

To remedy this shortcoming, Japanese document No 163 562 (1986), BRIDGESTONE CO, proposes a battery with an electroconductive polymer cathode and an anode of carbon material which dopes upon charging with cations. As such carbon materials pyrolyzed cellulose or phenolic resins

with conductivities above 10^{-4} S/cm are convenient.

The cathode material disclosed in this document includes polyaniline, polyphenylene, polyfuran, polypyrrole and others. Electrolytes to be used here include alkali metal salts of ClO_4^- , PF_6^- , AsF_6^- , BF_4^- , CNS^- , SO_4^{2-} and the like in solvents such as propylene and ethylene carbonate, benzonitrile, acetonitrile, tetrahydrofuran (THF), γ -butyrolactone, dioxane, MeCl_2 , trialkyl-phosphates and -phosphites, DMF, DMSO, dichloroethane, chlorobenzene and the like. In a working embodiment of this document, 2.7 mg of carbon textile material were doped for 12.5 hrs at $50 \mu\text{A}$ in a LiClO_4 /propylene carbonate solution against a polyaniline electrode. The charging capacity was 98 Ahr/kg of polyaniline, 233 Ahr/kg of carbon and 70 Ahr/kg of both electrode materials. The open circuit voltage was 3.8 V, and the cell voltage was 3.2 V under $50 \mu\text{A}$ discharge current. The final cell voltage was 2V and after 50 recycles, no metallic Li was deposited on the anode. The coulomb efficiency is indicated to be 86%.

Japanese document 62-176 046 (1987), application 15324 (1986), MITSUBISHI CHEM. IND. & SANYO ELECTRIC, discloses secondary batteries in which either the anode or the cathode or both are made of electroconductive polymers, inter alia, polypyrrole and polythiophene, said polymers being deposited into porous substrates to avoid them becoming disintegrated under use conditions. This document also discloses in its introductory part the prior existence of earlier batteries in which both electrodes are made of electroconductive polymers, namely in Japanese Publication No 216 471 (1985).

The porous substrates indicated in JP-62-176 046 include expanded metals and alloys such as Ni, Ni-Cr, Ni-Cu, Ni-Fe-Co, Fe-Cr, Cu, Fe, Pb, Cd, Au, Ag and others. Embodiments relate to cells in which the anode is of lithium and the cathode of electropolymerized pyrrole. Capacities of 28 mAhr/cm^2 are reported after charging under 7 mA/cm^2 in solutions of LiClO_4 in propylene carbonate. No workable details are however given for cells in which both electrodes are of polypyrrole.

Japanese document No 61-128478, applications No 59-250046 (1984), TOYOTA MOTOR CORP., reports a method for the production of negative electrodes of electrically conductive polymers, namely polypyrrole. This document also reports in its introductory part that polythienylene has been previously doped with quaternary ammonium ions to form an "n" type electroactive material, this being disclosed in the following Journal: Denki Kagaku 52 (1984), 80-81, edited by the Japanese Electrochemistry Association; however, the doping was reported not extensive. The materials reported

in JP-61-128478 include alkali metal trifluoromethane-sulfonate, BF_4^- and PF_6^- solutions in acetonitrile, DMF, propylene carbonate, THF, hexamethyl-phosphoramide and the like as electrolytes. The electrode collector substrates can be made of Pt or C-fibers. In an embodiment of this document, a graphite fiber sheet was coated electrolytically with pPy in a 0.2 M solution of pyrrole in acetonitrile (0.2 M $\text{Bu}_4\text{NCF}_3\text{SO}_3$ as supporting electrolyte), a Pt sheet being used as the negative counterelectrode. Hence, the obtained pPy electrode was a positively charged, anion doped material. This polypyrrole electrode was then converted to a negatively charged material by immersing into a 0.2 M Et_4NClO_4 solution in DMSO and charging against a Pt counterelectrode under 1-10 mA for 1 hr or more. The doping ratio indicated reached 10 mole % calculated on pPy and a terminal discharge voltage of 1.5 V versus the Ag/AgCl couple was reported.

When the present inventors attempted to repeat the foregoing experiments, they noted that the reported results were not attained; for instance the amount of charging and doping was insignificant and the anode thus conditioned could not be used in the manufacture of commercially workable batteries.

Hence the present inventors attempted to correct the aforementioned deficiencies and, after painstaking efforts, they obtained excellent results by improving both the structure of the anode and the conditioning technique. This is defined in the annexed claims.

It is interesting to note that although the new structure, i.e. at least one polypyrrole layer and at least one ion exchange resin layer over one another, is a key feature for the negative electrode of the invention (the anode), the same structure may also suit the positive electrode although it is not a must. The reasoning here (although not binding legally) is that the ion exchange resin layer forms a barrier at the anode and prevents its being undoped (discharged) spontaneously by the anions in the electrolyte, thus strongly improving the self-discharge protection characteristics. The reason why an alternating charging current provides so much enhanced conditioning efficiency (which may exceed 0.1 electron per pyrrole unit) has not been explained yet.

The invention is now explained in detail with reference to the annexed drawing in which:

Fig. 1 illustrates schematically a cell arrangement to be used for conditioning electrodes according to the invention.

Fig. 2 is a graph representing the potential of a polypyrrole coated electrode upon attempted charging with negative DC current.

Fig. 3 is a graph representing a charge and

discharge cycle for a polypyrrole coated negative electrode conditioned according to the invention.

The cell represented in fig. 1 comprises a container 1 filled with an electrolyte solution 2, i.e. a solution of a supporting salt like LiClO_4 in a polar organic solvent like propylene carbonate. Two main electrodes 3 and 4, respectively, are immersed in the electrolyte solution 2. The electrodes 3 and 4 are made of a current collecting material, e.g. metal, including Ni-sponge, or graphite, coated with layers 3a and 4a of polypyrrole. The electrode 3a further comprises a layer of ion exchange resin 3b, for instance a resin with sulfonate groups like Amberlite® or Nafion®. It should be noted that in the presently illustrated case, the electrode 3 is used as the negative electrode, and electrode 4 as the positive one. It should also be noted that if the collector material of electrode 4 is of carbon or graphite capable to form intercalates with the electrolyte anions, the layer of polypyrrole 4a can be omitted. Finally, in the instant illustrated embodiment, the electrode 4 with a polypyrrole layer could also be optionally provided with a layer of ion exchange resin, whereby the two electrodes would be formally symmetrical.

The present cell further comprises a reference electrode 5 which can be any conventional reference potential element. Since the present embodiment operates in a lithium salt solution a lithium foil reference electrode is convenient as it will provide a Li/Li^+ couple to be used as reference potential. The three electrodes in the system are connected to a potentiostat instrument 6, i.e. a conventional circuit which can continuously control and record (via a display or recorder not represented) the current (charge and discharge) in the main electrode circuit (this is measured on ammeter 7) as well as the voltage between the electrodes 3 and 4 and that relative to the reference couple 5.

The polypyrrole coating of the electrodes can be obtained conventionally, for instance by mechanically coating (pressing or painting) with chemically prepared polypyrrole. Polypyrrole can be prepared for instance by oxidizing pyrrole monomer with a ferric salt in aqueous or anhydrous media as disclosed in co-pending WO 87/01504 or by electrooxidation. A convenient way to do this is to dip a metal, including Ni-sponge or carbon collector plate or sheet in an aqueous solution of pyrrole and an electrolyte salt, for instance tosylate or mesylate, and submit the collector to anodization against a counterelectrode, of, for instance, an inert metal like platinum. A layer of positively charged (p) polypyrrole will then precipitate on the collector, doping being achieved here by the tosylate ions. In the embodiment of fig. 1, both electrodes 3 and 4 can be obtained this way. Then, electrode 3 is further coated with a film of ion

exchange resin, for instance by dipping into a solution or suspension thereof and thereafter drying. Of course, forming a new polypyrrole film over the resin and applying a new resin layer over the polypyrrole can be repeated to obtain a multilayer structure. Otherwise, the electroprecipitation of pPy can be brought about in the presence of a solution or dispersion of the ion exchange resin, whereby a multi-monomolecular layer structure will result.

For conditioning the electrode 3 as an anode, the latter should be first undoped by removing the positive charges and doping anions and then reloaded with electrons. As said before, using DC as disclosed in JP 61-128478 for effecting conditioning was ineffective as depicted in fig. 2.

In the experiment illustrated by fig. 2, a negative current (1 mA/cm²) was applied to electrode 3 for a period of about 30 min while recording the potential relative to the reference electrode (in the graph the origin corresponds to the reference potential of a saturated calomel element). So the initial potential was more than 5 Volt versus the Li/Li⁺ reference. Undoping did proceed smoothly (letter A) then a strong dip was observed and the potential progressively decreased beyond that of Li/Li⁺. After ~30 min the cell was allowed to discharge, whereby the negative electrode returned instantaneously to neutral (letter D) showing that the coulomb efficiency was substantially nought.

However when the conditioning was effected by a series of alternating negative and positive pulses (i.e. rapidly changing charging and discharging current), the electrode was efficiently converted to an electronegative electrode (coulomb efficiency exceeding 0.1 e/pyrrole unit) and excellent long-term cycling behaviour was noted. This is illustrated in fig. 3 which shows the typical charge/discharge cycle of such conditioned electrode in terms of voltage against the Li/Li⁺ couple with time under current densities of about 1 mA/cm². The considerable symmetry between the two legs of the curve can be noted, this symmetry being conserved for more than 100 cycles, which indicates excellent stability of the electrode materials. This is probably due to the efficiency of the ion exchange resin membrane in preventing the anions in the electrolyte from discharging at the anode.

The parameters pertaining to the alternating conditioning current in this invention vary between wide limits.

Preferably the frequency is comprised between about 0.1 and 100 Hz but this can be exceeded if necessary.

The average current (rms) is preferably in the range of 5 - 500 mA/cm².g but again these limits can be exceeded depending on electrode construction, thickness of the active layers and structure of the coatings. The negative pulses should exceed

the positive pulses by preferably at least 10% but can go to an upper limit of 3 or 4 times. It should be noted that the unbalance of the negative pulses versus the positive ones may not necessarily be in terms of intensity values but can also be in terms of time, i.e. for instance the intensities may be the same but the negative pulses may last longer than the positive pulses, e.g. 10% longer or twice as long, or the like. This distribution of the pulses can be effected conventionally by usual electronic means with which skilled ones are familiar and which need not be discussed in detail here.

The other parameters like selection of cell solvents, supporting salts, electrode collector materials are all conventional and in conformity with the data from the prior art (see the references cited in the introduction).

The examples below illustrate the invention.

Example 1

An electrode made of a bundle of strands of about 10.000 graphite fibers (SEROFIM, Gennevilliers, France), size 30 x 2 mm, thickness 2 mm was connected to a stainless steel current lead wire and dipped into a 1 molar aqueous solution of pyrrole containing 0,5 moles/L of sodium tosylate. The lead wire was protected against attack by the electrolyte. Naturally, other electroconductive materials, such as Pt, Ni, Cu and the like can also be used as lead wires.

A positive current (counterelectrode, a platinum plate of 40 x 10 mm) of 10 mA/cm² was applied to the carbon electrode for 1 hr, whereby a quantity of about 20 mg of polypyrrole doped with tosylate ions was deposited thereon as a black layer (current yield about 2 g/Ahr). The electrode thus doped in positive form can be stored dry for any period of time.

The above polypyrrole coated electrode was then coated with a layer of NAFION® by dipping into a 50% by weight solution or suspension of this material (commercially available from Aldrich Chemical Co., Milwaukee, WI, USA) and allowed to dry in air. This provided an approximately 50 μm layer of ion-exchange resin over the polypyrrole. It should be noted that these operations can be repeated several times and that the order of deposition of the layers (polypyrrole and NAFION®) can be reversed. Other commercial ion-exchange resins are also convenient.

A NAFION® coated polypyrrole electrode as prepared by the foregoing procedure and another larger polypyrrole electrode (not carrying a NAFION® overcoat) were used to make a cell of the kind illustrated in fig. 1. The electrolyte was a 1 molar solution of LiClO₄ in propylene carbonate.

For conditioning, an alternating current ($f = 50$ Hz) with 1 mA negative pulses and 0.5 mA positive pulses was applied until the voltage was about equal to the reference (Li/Li^+); this corresponds to about -2 V with respect to the H/H^+ standard potential.

Then the cell was allowed to discharge through the potentiostat 6 as indicated earlier to give the voltage/current curve depicted in fig. 3. Afterwards, the cycles of charge and discharge (DC only) could be repeated an indefinite number of times (>150 times) without significant loss of electrode performance. The initial charge of more than 0.6 C could be steadily increased to more than 5 C between 0.03 and 2 V, showing the remarkable advantages of the invention.

Example 2

A piece of fine-mesh expanded Ni screen was cut so as to provide a circular current collector. 10 mg of chemically prepared polypyrrole (tosylate-doped) was pressed under 15 t pressure into this screen. A nickel wire was the current lead; it was welded to the screen beforehand. A Nafion coating was applied to this electrode by dipping into a Nafion® solution (see Example 1) and allowing to dry. After complete drying, the electrode was arranged as shown in Fig. 1 using an electrolyte and a counterelectrode like in Example 1 to make a complete cell. Again the counterelectrode was larger than the main electrode so any limitations in performance are attributable to the structure with Nafion.

The electrolyte was 1 M LiClO_4 in a mixture of 80% propylene carbonate and 20% ethylene carbonate. For conditioning, 100 pulses of alternating direction (0.5 mA negative, 0.3 mA positive) were applied. The potential of the electrode tested as battery anode were observed during the pulses. It shifted in the negative direction, first slowly and then more markedly, until the negative end potential reached during pulses was in the vicinity of the Li/Li^+ potential.

After conditioning, the cell was able to sustain charge-discharge cycles in which the "negative", i.e. the nickel-polypyrrole-Nafion structure, functioned with a discharging capacity increasing from 15 C/g to over 80 C/g of active material with increasing number of cycles between 0.01 and 1.8 V vs Li/Li^+ . The testing was carried to about 40 cycles, the faradaic round trip efficiency was 90 - 96%

Claims

1. Rechargeable storage battery having cells containing a non-aqueous alkali-metal salt solution electrolyte and current collector substrates coated with one or more polypyrrole layers as anode and cathode electrodes, characterized in that at least the anode comprises one or more layers of ion-exchange resin, the polypyrrole and ion-exchange resins layers being placed over each other.

2. A method of conditioning the anode of the battery of claim 1, in which said anode is immersed in a non-aqueous lithium salt solution with a counterelectrode and a conditioning current is applied to said anode against said counterelectrode, characterized in that the conditioning current comprises balanced or unbalanced alternating positive and negative pulses.

3. The method of claim 2, characterized in that the conditioning current comprises unbalanced alternating positive and negative pulses.

4. The method of claim 3, wherein the negative pulses predominate over the positive pulses by 10% or more.

5. The method of claim 4, wherein the negative pulses are of 1 - 500 mA/cm^2 g of polypyrrole and the positive pulses are about half the negative pulses.

6. The method of claim 3, wherein the negative pulses last longer than the positive pulses.

7. The method of claim 3, wherein the anode current collector is made of carbon, the ion-exchange resin is a perfluorinated sulfonic ion-exchange resin and the electrolyte is LiClO_4 in a polar organic solvent.

8. The storage battery of claim 1, wherein the polypyrrole and ion-exchange resin layers are at least mono-molecular thick.

9. The storage battery of claim 1, wherein at least the anode current collector is of Ni-sponge.

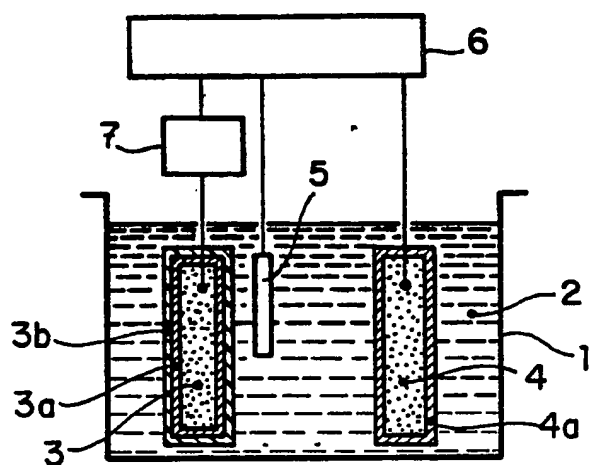


FIG. 1

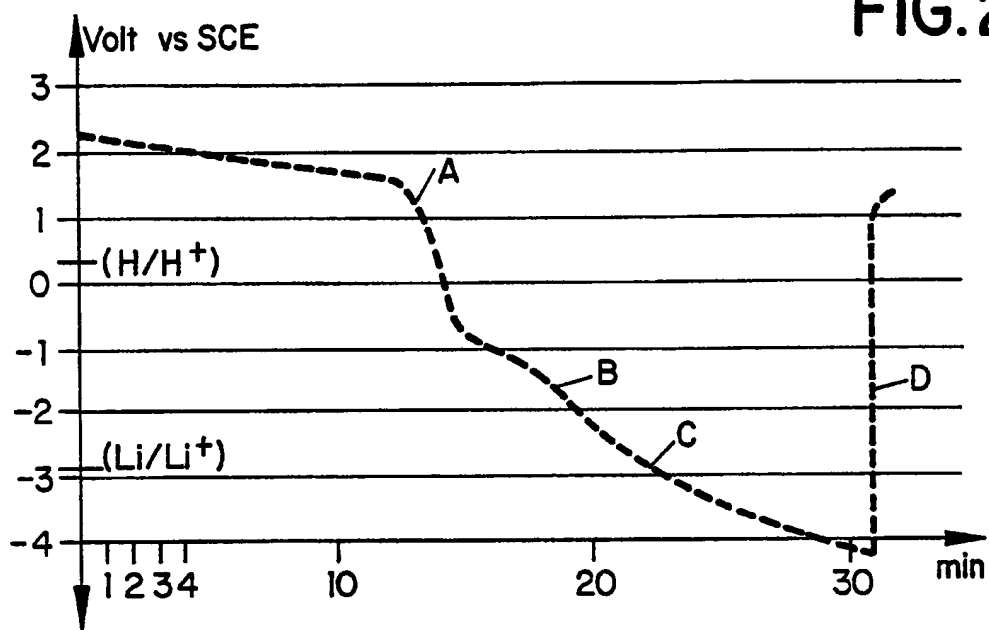


FIG. 2

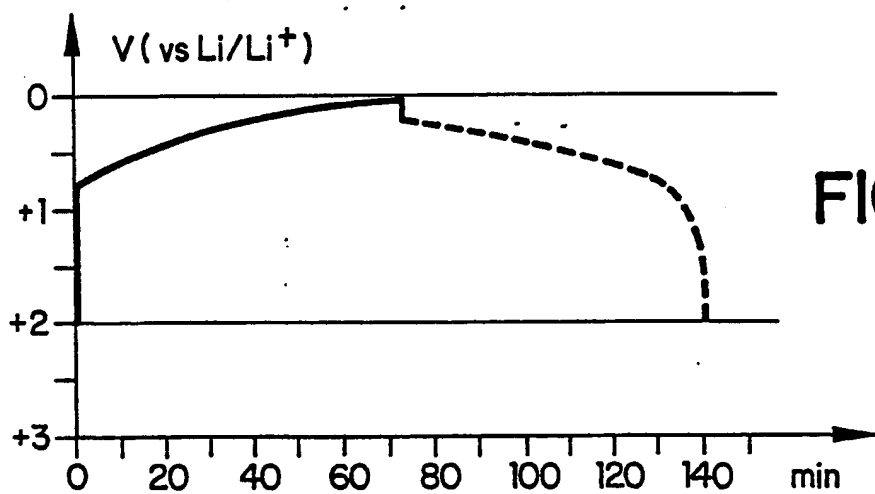


FIG. 3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 81 0440

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 5)
X	JOURNAL OF PHYSICS D/APPLIED PHYSICS, vol. 21, no. 7, 14th July 1988, pages 1043-1054; G. BIDAN et al.: "Conductive polymers with immobilised dopants: ionomer composites and auto-doped polymers - a review and recent advances" * Abstract; page 1044, line 1 - page 1049, paragraph 1 * ---	1	H 01 M 4/60 H 01 M 10/40
X	J. ELECTROCHEM. SOC., vol. 135, no. 5, May 1988, pages 1132-1137; TAKAYUKI HIRA et al.: "Electrochemical behaviors of polypyrrole, poly-3-methylthiophene, and polyaniline deposited on nafion-coated electrodes" * Abstract; page 1134, left-hand column, paragraph 2 - right-hand column, paragraph 4; page 1136 * ---	1,8	
X	J. CHEM. SOC. CHEM. COMMUN., 1987 (5), pages 327-328; T. SHIMIDZU et al.: "A novel type of polymer battery using a polypyrrole-polyanion composite anode" * Whole document * ---	1	TECHNICAL FIELDS SEARCHED (Int. Cl.5) H 01 M 4/60 H 01 M 10/40
A	PATENT ABSTRACTS OF JAPAN, vol. 12, no. 265 (E-637)[3112], 23rd July 1988; & JP-A-63 48 750 (SANYO ELECTRIC CO., LTD) 01-03-1988 * Whole document * ---	2-6	
A	EP-A-0 315 559 (UNIVERSIDAD DEL PAIS VASCO) * Whole document * ---	2-7	
		-/-	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 20-02-1990	Examiner DE VOS L.A.R.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 143 968 (WOLF JAMES F.) * Abstract; page 3, line 35 - page 9, line 27 * ---	1	
A	EP-A-0 104 726 (RAYCHEM LTD) * Abstract; page 3, line 10 - page 6, line 32; page 14, example 8 * ---	1,7	
A	J. CHEM. SOC., CHEM. COMMUN., 1986, pages 1636-1638; PIERRE ALDEBERT et al.: "New chemical synthesis of mixed conductivity polymers" * Whole document * ---	1	
A	DE-A-3 326 193 (NIPPON DENSO CO., LTD) * Claims 1,2,6 * ---	1,9	
A	PATENT ABSTRACTS OF JAPAN, vol. 13, no. 176 (E-749)[3524], 25th April 1989; & JP-A-1 6383 (SONY CORP.) * Whole document * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 20-02-1990	Examiner DE VOS L.A.R.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			